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High Thermal Conductivity Fibers from PBO

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13. ABSTRACT (Maximum 200 words)

Carbon fibers produced from PBO develop three dimensional ordering that is better than other polymeric precursors, such as PAN. The low electrical resistivities achieved by PBO-based carbon fibers implies high thermal conductivity. Stabilization of the polymer fiber is not needed to obtain the 3-D ordering and low electrical resistivity. This ability to develop into a high thermal conductivity fiber without stabilization may be particularly attractive for use in carbon-carbon composites. The elimination of one carbonization cycle in the manufacture of CC composites may reduce the production cost.

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FY96 End of Fiscal Year Letter

SEPTEMBER 30, 1995 - OCTOBER 1, 1996

ONR CONTRACT INFORMATION

Contract Title: HIGH THERMAL CONDUCTIVITY FIBERS FROM PBO

Performing Organization: Clemson University

Principal Investigator: Dan Edie [Ph. (864) 656-3056, FAX (864) 656-0784]

Contract Number: N00014-94-1-1159 (CU REF: 05-5911)

ONR Scientific Officer: A. K. Vasudevan

A. Research Goals

The objective of the project is to examine the conversion of poly p-phenylenebenzobisoxazole (PBO) to carbon fiber. The aromatic, rigid-rod backbone of the polymer enables the carbonized fiber to develop a three-dimensionally ordered structure without stabilization. Because of this structure, PBO fibers appear capable of developing relatively high thermal conductivities when carbonized.

B. Significant Results

Carbon fibers produced from PBO develop three dimensional ordering that is better than other polymeric precursors, such as PAN. The low electrical resistivities achieved by PBO-based carbon fibers implies high thermal conductivity. Stabilization of the polymer fiber is not needed to obtain the 3-D ordering and low electrical resistivity. This ability to develop into a high thermal conductivity fiber without stabilization may be particularly attractive for use in carbon-carbon composites. The elimination of one carbonization cycle in the manufacture of CC composites may reduce the production cost.

The studies performed the first year demonstrated the unique ability of PBO fiber to be carbonized without prior stabilization. Further, the experiments showed carbon fibers manufactured from stabilized fibers had no significant affect on the mechanical properties when compared to carbon fibers produced from unstabilized fibers.

The transition between carbonization and graphitization is not clearly defined. The crystalline growth and three-dimensional ordering associated with graphitization may begin prior to the final mass release. Further, many carbonaceous materials never develop graphitic order. Thus, general conclusions cannot be drawn about the location of the transition boundary.

X-ray diffraction profiles of the as-received and carbonized fibers confirm that the fibers pass from their initially ordered liquid crystalline state to an amorphous form at approximately 600 °C. Ultimately, the disordered carbon remnants begin forming a turbostratic structure. The turbostratic structure continues to develop throughout the graphitization process.

At temperatures above 1600 °C, carbonized PBO fibers begin to develop three-dimensional order. As this order develops, the average interlayer spacing between graphene planes decreases. Fibers with interlayer spacings greater than 3.42 angstroms are considered disordered or turbostratic, while fibers with interlayer spacings less than 3.42 angstroms are considered ordered, or graphitic.

Figure 1 shows that carbonized PBO fibers become increasingly ordered with elevated treatment temperatures. The first signs of long range order appear at 1600 °C, where the average interlayer spacing is nearly 3.45 angstroms. The fiber develops more order as temperatures rise, finally becoming "graphitic" at 2400 °C.

Crystalline graphite has a mean interlayer spacing of 3.35 angstroms, which indicates that the carbonized PBO fiber still does not approach the crystallinity of graphite. However, PBO displays more graphitic order than other polymeric precursors such as PAN.

Electrical resistivity tests were performed on the carbonized PBO fibers. Ideally, the electrical resistivity should decrease when the fiber is treated at higher temperatures because of the increased molecular ordering associated with elevated treatment temperatures. However, Figure 2 shows that the electrical resistivity of PBO-based

carbon fiber decreased with increasing temperature only to 1400 °C. Above this temperature an increase in electrical resistivity is observed.

The electrical resistivity of PBO-based carbon fibers produced in a continuous operation at 2200 °C was found to be approximately 9 $\mu\Omega$-m. This value compares favorably with essentially all carbon fibers produced from polymer precursors. Additionally, the resistivity places PBO in the conductivity range of some commercial mesophase pitch-based carbon fibers.

C. Future Research

The kinetics of the carbonization of the polymeric fiber will be studied and modeled.

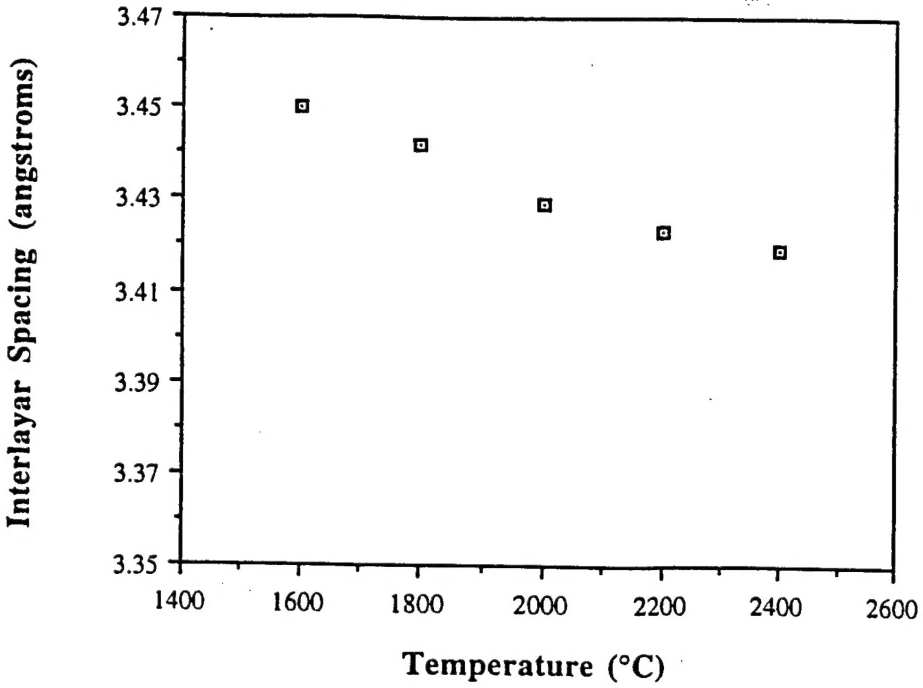

Figure 1 The influence of treatment temperature on interplanar spacing

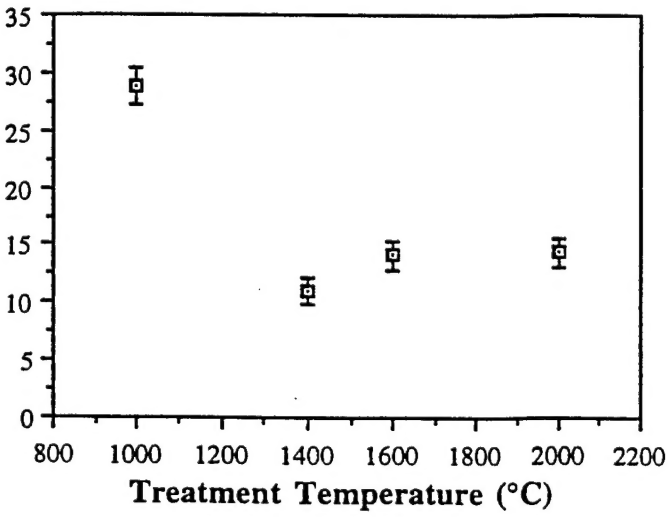

Figure 2 The influence of treatment temperature on the electrical resisitivity of PBO-based carbon fibers

D. List of Publication /Reports/Presentations

1. Papers Published in Refereed Journals

"Kinetics of Carbonization and Graphitization of PBO Fiber," J. A. Newell, D. D. Edie, and E. Loren Fuller Jr., Journal of Applied Polymer Science, **60**, pp. 825-832 (1996).

"Factors Limiting the Thensile Strength of PBO-Based Fibers," J. A. Newell and D. D. Edie, Carbon, in press.

2. Non-Refereed Publications and Published Technical Reports

"High Thermal Conductivity Carbon/Carbon Composites Made from a Novel Process," C. M. Mundt and D. D. Edie, Carbon '96, Proceedings of the 7th International Conference on Carbonl, New Castle-upon-Tyne, England, July 7-12, 1996, pp 709.

3. Presentations

a. Invited

b. Contributed
(See item 2 above)

4. Books (and sections thereof)

E. Lists of Honors/Awards

Name of Person Receiving Award	Recipient's Institution	Name, Sponsor and Purpose of Award
Dan D. Edie	Clemson University	Plenary Lecture at 23rd Biennial Conferencen on Carbon

F. Participants

James Newell, completed Ph.D. in Chemical Engineering and graduated from Clemson University in December, 1994.

Chad Mundt, currently a Ph.D. candidate in Chemical Engineering and should graduate from Clemson University in December, 1997.

G. Other Sponsored Research During Grant Period

This Grant

"High Thermal Conductivity Fibers from PBO," Sponsored by ONR, 0% of time, $91,176/yr, 7/31/94 to 8/1/97.

Other Grants

"Supercritical Extraction for High Thermal Conductivity Fibers," Sponsored by ARO, $100,000/yr, 15% of time, 9/1/94 to 8/31/97.

"Studies of Fiber Matrix Bonding & Physical Properties of C/C Composites made with Carbon Fiber of Different Morphologies," Sponsored by NSF, $11,000/yr, 0% of time, 9/1/96 to 8/31/99.

"Development of High Thermal Conductivity Ribbon-Shaped Fibers," Sponsored by ONR, $250,000/yr, 17% of time, 12/18/95 to 4/30/98.